

PATENT SPECIFICATION

(11) 1293331

NO DRAWINGS



- (21) Application No. 1026/70 (22) Filed 8 Jan. 1970
 (31) Convention Application No. 790830 (32) Filed 13 Jan. 1969 in
 (33) United States of America (US)
 (45) Complete Specification published 18 Oct. 1972
 (51) International Classification C08G 31/14
 (52) Index at acceptance
 C3T 6D3 6D5 6D6 6F2 6G7D 6G7F 6G7G
 (72) Inventor LAWRENCE MARLIN

(54) ADDITION PROCESS FOR PRODUCING SILOXANE ALCOHOLS

(71) We, UNION CARBIDE CORPORATION, a Corporation organised under the Laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Siloxane-polyoxyalkylene block copolymers have found wide acceptance as foam stabilizers in the production of polyurethane foams. A preferred class of such block copolymers are those wherein the blocks are linked by silicon to carbon bonds. These preferred block copolymers ("non-hydrolyzable" block copolymers) exhibit a greater degree of hydrolytic stability than similar block copolymers in which the blocks are linked by silicon to oxygen to carbon bonds. It is at times desirable to employ such preferred non-hydrolyzable block copolymers as foam stabilizers for polyurethane foams intended for use as thermal insulation. In that use, it is desirable that the polyurethane foams have mostly or exclusively closed cells rather than open cells as open cells provide a relatively thermally conductive gas path through the foam.

In the production of closed cell polyurethane foams for use as thermal insulating materials, siloxane-polyoxyalkylene block copolymers wherein the polyoxyalkylene blocks contain alcoholic hydroxyl end groups are particularly useful as such block copolymers are compatible with premixtures of the polyols, blowing agents and catalysts usually formulated and stored prior to reaction with a polyisocyanate to produce the foams.

A widely accepted procedure for producing non-hydrolyzable siloxane-polyoxyalkylene block copolymers wherein the polyoxyalkylene blocks contain alcoholic hydroxyl end groups involves reacting a siloxane containing an SiH group with a linear polyoxyalkylene polymer whose linear chain is terminated at one end

with an alkenyl group and at the other end with either an alcoholic hydroxyl group or a group readily convertible to an alcoholic hydroxyl group. The latter reaction is conducted in the presence of a chloroplatinic acid catalyst (e.g., chloroplatinic acid, its hydrate or a complex of chloroplatinic acid). The SiH groups add to the alkenyl groups to produce the block copolymer. When the polyoxyalkylene reactant contains an alcoholic hydroxyl end-blocking group, such groups can also react to some extent with the SiH groups thereby decreasing the content of the desired hydroxyl groups in the block copolymer product. This side reaction also undesirably increases the viscosity of the block copolymer product by crosslinking some of the siloxane blocks. When the polyoxyalkylene reactant contains an end group readily convertible to a hydroxyl group, the undesirable side reaction of the hydroxyl group and SiH groups does not occur but the block copolymer formed therefrom must be further processed to regenerate the hydroxyl groups.

Siloxane-polyoxyalkylene block copolymers nominally free of alcoholic hydroxyl groups are also produced by a chloroplatinic acid catalyzed addition reaction between a siloxane containing SiH groups and a polyoxyalkylene polymer. In such cases, the polyoxyalkylene polymer reactant is usually a linear polymer whose linear chain is theoretically terminated at one end by an alkenyl group and at the other end by a monovalent organic group free of aliphatic carbon to carbon multiple bonds (e.g., an alkoxy group or an acyloxy group). In actual practice, however, it is difficult to prepare such polyoxyalkylene polymer reactants free of minor amounts of polyoxyalkylene polymers terminated with an alkenyl group and, rather than the desired monovalent organic group, a hydroxyl group. When these polyoxyalkylene polymers are reacted with siloxanes containing SiH groups, the hydroxyl terminated impurities can react with SiH to produce crosslinks in the siloxane-polyoxyalkylene block copolymer with the result that

[Price 25p]

viscosity of the copolymer is higher than it would otherwise be.

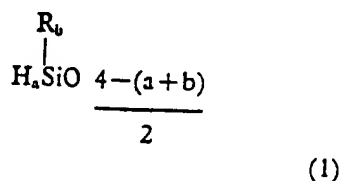
Similar difficulties are encountered when other olefinically unsaturated alcohols (e.g., allyl alcohol and the monoallyl ether of trimethylol propane) are reacted with hydrosiloxanes by known addition processes. That is, the hydroxyl groups tend to react with SiH to the extent that the final products may be relatively useless gels.

This invention provides a process for producing a siloxane-alcohol having an alcoholic hydroxyl group linked to a silicon atom through an alkylene group containing at least two carbon atoms, which process comprises forming a mixture of a siloxane reactant that contains an SiH group and that is free of aliphatic carbon to carbon multiple bonds, a reactant that contains an alcoholic hydroxyl group and an olefinic double bond, a basic compound, said basic compound being a compound (a) that is water-soluble and imparts a pH from 8.0 to 12.0 to water at 0.1 N concentration or (b) that is water-insoluble but soluble in a mixture of six parts by volume of water and ten parts by volume of isopropanol and imparts a pH from 8.0 to 12.0 to said mixture at 0.1 N concentration, and a chloroplatinic acid catalyst (as hereinafter defined) for the addition of the SiH group to the olefinic bond and thereafter maintaining the mixture at a temperature at which the addition occurs to produce the siloxane alcohol.

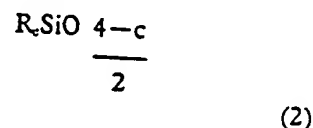
In a preferred embodiment, this invention provides a process for producing a siloxane-polyoxyalkylene block copolymer having a polyoxyalkylene block that contains an alcoholic hydroxyl group and that is linked to a silicon atom of a siloxane block through an alkylene group containing at least two carbon atoms, said process comprising (1) forming a mixture of a siloxane reactant that contains an SiH group and that is free of aliphatic carbon to carbon multiple bonds, a polyoxyalkylene polymer reactant that contains an alcoholic hydroxyl group and an olefinic double bond, a basic compound, said basic compound being a compound: (a) that is water-soluble and imparts a pH from 8.0 to 12.0 to water at 0.1 N concentration or (b) that is water-insoluble but soluble in a mixture of six parts by volume of water and ten parts by volume of isopropanol and imparts a pH from 8.0 to 12.0 to said mixture at 0.1 N concentration, and a chloroplatinic acid catalyst for the addition of the SiH group to the olefinic bond and (2) maintaining the mixture at a temperature at which the addition occurs to produce the block copolymer without any substantial reaction of the hydroxyl group.

The process of this invention is generally applicable to siloxane reactants containing SiH groups and free of aliphatic carbon to carbon

multiple bonds (i.e., free of acetylenic and olefinic bonds). Such siloxane reactants include siloxanes containing both groups represented by the formula:

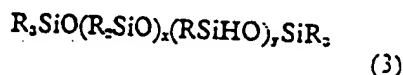


and groups represented by the formula:



wherein R is a monovalent hydrocarbon group free of aliphatic carbon to carbon multiple bonds, *a* has a value of 1 or 2, *b* has a value of 1, 1 or 2, (*a*+*b*) has a value of 1, 2 or 3 and *c* has a value of 1, 2 or 3.

Preferred siloxane reactants for use in the process of this invention are those represented by the average formula:



wherein R is a monovalent hydrocarbon group free of aliphatic carbon to carbon multiple bonds, *x* has a value from 0 to 200 inclusive and *y* has a value from 1 to 50 inclusive.

Typical of the groups represented by R in formula (1), (2) and (3) are the linear alkyl groups (e.g., the methyl, ethyl, propyl, butyl, amyl, octadecyl and dodecyl groups), the cyclic alkyl groups (e.g. the cyclobutyl, cyclopentyl and cyclohexyl groups), the aralkyl groups (e.g., the benzyl and beta-phenyl ethyl groups), the alkaryl groups (e.g., the tolyl and xyl groups) and the aryl groups (e.g., the phenyl and naphthyl groups).

The process of this invention is generally applicable to reactants containing both an alcoholic hydroxyl group and an olefinic double bond.

Suitable alcohol reactants include alkenols (e.g., allyl alcohol, methallyl alcohol, butenol, pentenol, etc.), alkenyl ethers of polyols and alkenyl ethers of polyoxyalkylene polymers.

Such alkenyl ethers of polyols include: trimethylolethane monoallyl ether; trimethylolpropane monoallyl ether; trimethylolbutane monoallyl ether; and other monoallyl ethers of other trimethylolalkanes as well as the analogous diallyl ethers such as trimethylolpropane diallyl ether. As a further illustration, suitable alkenyl ethers starting materials are the mono, di-, and triallyl ethers of pentaerythritol. As a still further illustration, suitable alkenyl ethers starting materials include the mono- and di-allylethers of hexanetriol,

2-ph
2-ph
prop
pance

10

15

20

25

30

85

90

95

100

105

110

40

115

Othe
process

2-ph
2-me
α,α
eth
dio

CH

* CH

* FCH₂

*prod
aer
**prod
per

CH₂

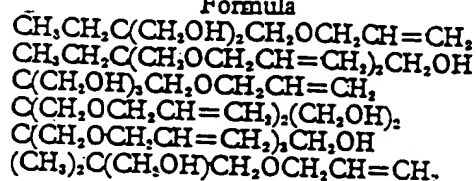
and alken

acetylenic and
etc include
s represented

2-phenyl, 2-allyloxymethyl propanediol-1,3,
2-phenyl, 2-hydroxymethyl 1,3-diallyloxy-
propane, 2-cyclohexyl, 2-allyloxymethyl pro-
panediol-1, 3 and 2-cyclohexyl, 2-hydroxy-

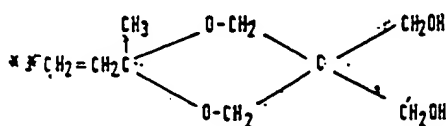
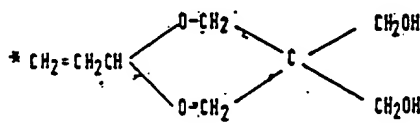
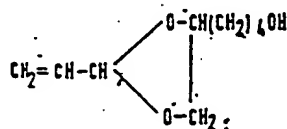
methyl 1,3 - diallyloxypropanediol. The
formulae of typical alkenyl ethers suitable for
use in the process of this invention are as fol-
lows:

Formula



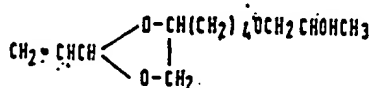
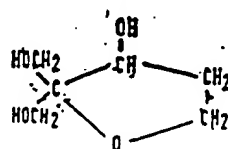
Other alkenyl ethers suitable for use in the
process of this invention are the following:

2-phenyl, 2-allyloxymethyl propanol;
2-methyl, 2-allyloxymethyl propanol;
 α,α - dimethylolethylbenzene monoallyl
ether (2-phenyl, 2-methyl, 1,3-propane-
diol monoallyl ether);



*produced by reacting acrolein and penta-
erythritol

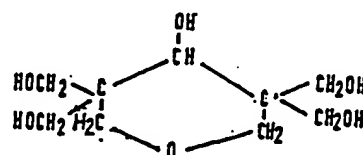
**produced by reacting methacrolein and
pentaerythritol alkenyl ethers of



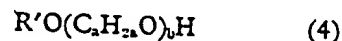
and alkenyl ethers of:

Name

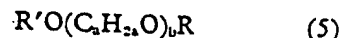
Trimethylolpropane monoallyl ether
Trimethylpropane di-allyl ether
Pentaerythritol monoallyl ether
Pentaerythritol diallyl ether
Pentaerythritol triallyl ether
Dimethylolpropane monoallyl ether
(2,2 - dimethyl - 1,3 - propanediol
monoallyl ether)
Trimethylolmethylbenzene mono-
allyl ether (2 - phenyl - 2 - allyloxy-
methyl propanediol - 1,3)
Trimethylolmethylbenzene diallyl
ether (2 - phenyl, 2 - hydroxy
methyl 1,3 - propanediol - diallyl
ether)



Preferred polyoxyalkylene polymer reactants
for use in this invention are those represented
by the average formula:

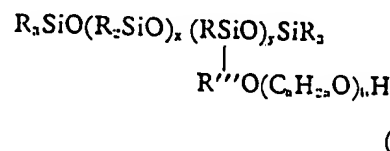


wherein R' is an alkenyl group (e.g. a vinyl,
allyl, butenyl, pentenyl or a decenyl group),
a has a value of at least 2 (preferably from 2
to 4 inclusive) and b has a value of at least 1
(preferably from 1 to 100 inclusive). Such
reactants can be used mixed with polymers
having the average formula:



wherein R, R', a and b have the above-defined
meanings.

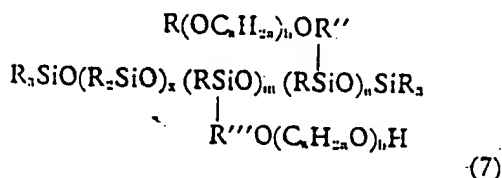
When the preferred reactants represented
by formulas (3) and (4) above are employed in
the process of this invention, the block co-
polymer produced by the process has the
average formula:



wherein R''' is an alkylene group derived
from the alkenyl group R' and R, a, b, x and
y have the above-defined meanings.

When reactants of formula (3) are reacted
with a mixture of reactants of formulas (4)

and (5) in the process of this invention, the resulting block copolymer has the average formula:



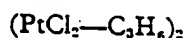
wherein R, R'', R''', x, a, b and n have the above-defined meanings.

Formulas (1) through (7) above can represent discrete chemical compounds or mixtures. In the latter case, they are average formulas. In these formulas, the symbols used need not have the same meaning at each occurrence in the molecule.

The basic compounds employed in the process of this invention include any of a wide variety of water-soluble materials that, at a concentration 0.1N, impart a pH of 8.0 to 12 to water and water-insoluble but water-isopropanol soluble materials that, at a concentration of 0.1N, impart a pH of 8.0 to 12 to water-isopropanol admixtures. Suitable basic compounds include bases (e.g. magnesium hydroxide) basic salts (e.g. sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, calcium carbonate, sodium borate, potassium bicarbonate), basic metal oxides (e.g. magnesium oxide), organic amines (e.g. hexadecyldimethylamine, triethylamine, tributylamine and 2-ethylhexyldimethylamine) and mixtures of trisodium phosphate and disodium hydrogen phosphate.

The term "chloroplatinic acid catalyst" as used herein is defined as a catalyst of chloroplatinic acid or of a compound derived from chloroplatinic acid.

The chloroplatinic acid catalysts employed in the process of this invention include chloroplatinic acid itself, chloroplatinic acid hydrate and complexes derived from chloroplatinic acid. Suitable complexes derived from chloroplatinic acid include: an aryl nitrile-platinum (II) halide complex, an alkyl nitrile-platinum (II) halide complex, an alkaryl nitrile-platinum (II) halide complex, an aralkyl nitrile-platinum (II) halide complex, and a haloaryl nitrile-platinum (II) halide complex;



where C_3H_5 is cyclopropane; $PtCl_2-Olefin$; $H(PtCl_2-Olefin)$; and a complex of chloroplatinic acid and nitrogen-containing or phosphorus-containing ligand. Such complexes are disclosed in US Patents 3159601; 3159662; 3188299; 3188300 and 3410886. The chloroplatinic acid catalyst can be employed dissolved in a suitable solvent such as alcohols (e.g. ethanol and butanol), and

ethers (e.g. tetrahydrofuran and ethylene glycol dimethyl ether).

The relative amounts of the siloxane reactant, polyoxyalkylene polymer reactant, basic compound and catalyst employed in the process of this invention are not narrowly critical. An amount of the polyoxyalkylene polymer reactant that provides an excess of olefinic groups is preferred as it ensures complete reaction of the more expensive siloxane reactant. The preferred amount of the basic compound is from 0.2 to 2.0 weight per cent based on the weight of the reactants. The preferred amount of the catalyst is that amount which provides from 5 to 100 parts of elemental platinum per million parts by weight of the reactants.

If desired, the process of this invention can be conducted in a solvent for the reactants. Suitable solvents include hydrocarbons such as toluene and polyoxyalkylene polymers having the formula:



wherein R, a and b have the above-defined meanings. The process is preferably conducted by maintaining the reactants at 40 to 120°C at atmospheric pressure. Where volatile materials are used, the process can be conducted at pressures above atmospheric pressure.

The block copolymers produced by the process of this invention are useful as foam stabilizers in the conventional one-shot process for producing polyurethane foams, especially closed cell rigid foams, from polyether polyols and polyisocyanates. In view of their relatively low viscosities and relatively high hydroxyl contents, the block copolymers produced by the process of this invention are more useful in producing such foams than block copolymers produced by prior processes from polyoxyalkylene polymers containing alcoholic hydroxyl groups and olefinic double bonds without control of pH.

The following examples illustrate the present invention:

In the Examples I and II appearing below, the block copolymers were produced according to the following general procedure. The siloxane reactant and the polyoxyalkylene polymer reactant were placed in a four-necked flask fitted with a still-head, stirrer, thermometer and sparge tube. The siloxane reactant was present in an amount that provided 1.0 SiH group per 1.3 allyl groups in the polyoxyalkylene polymer reactant. Toluene was added to the flask in an amount equal to 50% of the weight of the reactants. The basic compound was then added to the flask in the amount indicated in the examples. The mixture so formed was sparged with nitrogen and heated to 55°C. Then sparging was discon-

tinued the mi-
parts b
by wei
5 then he
stantial
minutes
by spar
product
10 polymer
the exce

Using

25 The reac
three dif
poses of
basic con
copolyme
results ar

30 Basic Con
Hexadecyl
amine
NaHCO₃
Na₂CO₃
None

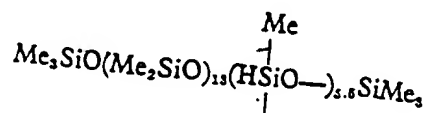
35 *Gels wer
40 repeated.
The ma
copolymer:

Me₃

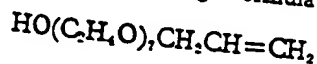
45 The reactive
Na₂CO₃ (1
general pro
that initial
added to t

tinued and chloroplatinic acid was added to the mixture in an amount that provided 70 parts by weight of platinum per million parts by weight of the reactants. The mixture was then heated at reflux until the SiH had substantially disappeared (e.g., for about thirty minutes). Thereafter the toluene was removed by sparging with nitrogen and the sparged product was filtered to isolate the block copolymer as the filtrate which also contained the excess polyoxyalkylene polymer.

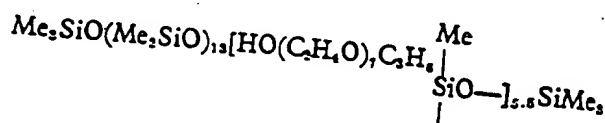
above, a siloxane reactant having the average formula:



was reacted with a polyoxyalkylene polymer reactant having the average formula:



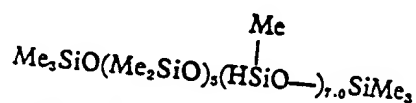
Using the general procedure described to produce a block copolymer having the average formula:



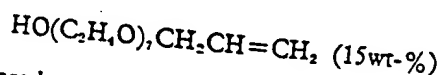
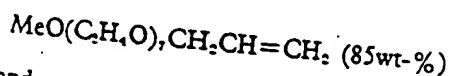
The reaction was repeated three times using three different basic compounds and, for purposes of comparison, a fourth time using no basic compound. The viscosities of the block copolymers so produced were measured. The results are shown in Table I below.

pounds are due to less crosslinking through the hydroxyl groups.

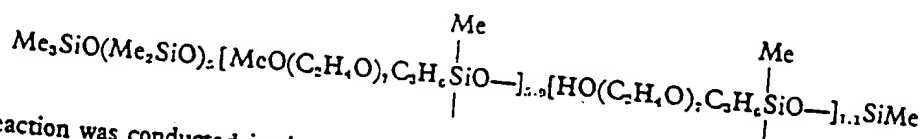
Example II
Using the general procedure described above, a siloxane reactant having the average formula:



was reacted with a mixture of polyoxyalkylene polymer reactants having the average formulas:



to produce a block copolymer having the average formula:



The reaction was conducted in the presence of Na_2CO_3 (1 wt-% based on the reactants). The general procedure was modified to the extent that initially only 50 parts of platinum were added to the flask. The additional 20 parts of

platinum were added after thirty minutes at reflux and refluxing was then continued for 20 minutes. The reaction was also conducted in the absence of Na_2CO_3 .

Table I

Basic Compound	Concentration (wt.-% based on reactants)	Copolymer Viscosity (centistokes at 25°C)
Hexadecyl dimethyl-amine	1.0	255
NaHCO_3	0.5	334
Na_2CO_3	1.0	273
None	0.0	4,000*

*Gels were produced when this reaction was repeated.

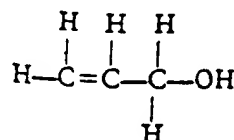
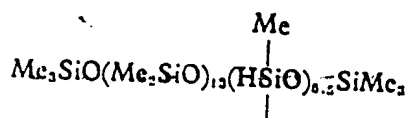
The markedly lower viscosities of the block copolymers produced using the basic com-

Table II

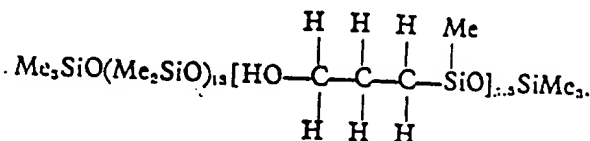
Na_2CO_3	Copolymer Viscosity (centistokes—at 25°C)	Wt-% Hydroxyl In Copolymer
Present	105	Calc. Obs.
Absent	127.5	0.53 0.6 ± 0.05
		0.53 0.08 ± 0.05

Again, the higher viscosity of the copolymer produced in the absence of the basic compound is due to crosslinking via the hydroxyl groups as indicated by the lower hydroxyl content of that copolymer.

Example III



to produce a siloxane alcohol having the average formula



The reaction was run with and without Na_2CO_3 as described below:

15 The siloxane reactant and the allyl alcohol were placed in a four necked flask fitted with a still-head, stirrer, thermometer and sparge tube. The siloxane reactant was present in the amount that provided one SiH group per 1.3 allyl groups. Toluene was added to the flask in the amount equal to 50% of the weight of the reactants. The basic compound was then added to the flask in the amount indicated in the table. The mixture so formed was sparged with nitrogen and heated to 55°C . Then sparging was discontinued and chloroplatinic acid was added to the mixture in an amount that provided 50 parts by weight of elemental platinum per million parts by weight of the reactants. The mixture was held at approximately 85°C . to avoid distilling allyl alcohol until substantially all the SiH was consumed. Thereafter the toluene was removed by heating to 130°C . under nitrogen sparge. The sparged product was filtered to isolate the siloxane alcohol as a filtrate. The viscosity of the siloxane alcohols were as follows:

Basic Compound	Concentration (wt. % based on reactants)	Product Viscosity ctsk at 25°C .
Na_2CO_3	1.0%	793
No Base	—	gel

45 The formation of the gel in the absence of the Na_2CO_3 indicates crosslinking through the hydroxyl groups.

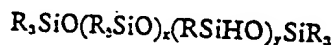
WHAT WE CLAIM IS:—

1. A process for producing a siloxane alcohol having an alcoholic hydroxyl group linked to a silicon atom through an alkylene group containing at least two carbon atoms, which process comprises forming a mixture of a siloxane reactant that contains an SiH group and that is free of aliphatic carbon to carbon

multiple bonds, a reactant that contains an alcoholic hydroxyl group and an olefinic double bond, a basic compound, said basic compound being a compound (a) that is water-soluble and imparts a pH from 8.0 to 12.0 to water at 0.1N concentration or (b) that is water-insoluble but soluble in a mixture of six parts by volume of water and ten parts by volume of isopropanol and imparts a pH from 8.0 to 12.0 to said mixture at 0.1N concentration, and a chloroplatinic acid catalyst for the addition of the SiH group to the olefinic double bond and thereafter maintaining the mixture at a temperature at which the addition occurs to produce the siloxane alcohol.

2. A process as claimed in claim 1 wherein the catalyst is chloroplatinic acid.

3. A process as claimed in claim 1 or claim 2 wherein the siloxane reactant is represented by the average formula

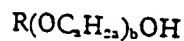


(1)

wherein R is a monovalent hydrocarbon group free of aliphatic carbon to carbon multiple bonds, x has a value from 0 to 200 inclusive and y has a value from 1 to 50 inclusive.

4. A process as claimed in any one of the preceding claims wherein the organic reactant is allyl alcohol.

5. A process as claimed in any one of claims 1 to 3 wherein the organic alcohol reactant is a polyoxyalkylene polymer represented by the average formula



(2)

wherein R is an alkenyl group, a has a value of at least 2 and b has a value of at least 1.

6. A process as claimed in claim 1 substantially as hereinbefore described in any one of Examples I to III.

7. A siloxane alcohol whenever produced

by a process as claimed in any one of the preceding claims.

- 5 8. Polyurethane foams including siloxane alcohol as claimed in claim 7 as a foam stabiliser.

BOULT, WADE & TENNANT,
34 Cursitor Street,
London EC4A 1PQ.
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

the aver- 10

contains an
an olefinic 55
said basic
is water-
3.0 to 12.0
or (b) that
mixture of 60
ten parts
parts a pH
0.1M con-
id lyst
mp is the 65
maintain-
which the
siloxane

1 wherein 70
1 or claim
represented

(1) 75

carbon group
multiple
50 inclusive
inclusive.
one of the 80
mic reactant

any one of
alcohol reac- 85
representen-

(2)

has a value
at 1. 90
substan-
any one
produced

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.